

CLAIMS

1. A method for producing a stabilized fluoropolymer which comprises producing said
5 stabilized fluoropolymer by subjecting a treatment target substance containing a sulfonic-acid-derived-group-containing fluoropolymer to a fluorination treatment, wherein said sulfonic-acid-derived-group-containing
10 fluoropolymer is a fluoropolymer containing $-\text{SO}_3\text{M}$ (in which M represents H, $\text{NR}^1\text{R}^2\text{R}^3\text{R}^4$ or $\text{M}^1_{1/\text{L}}$; R^1 , R^2 , R^3 and R^4 are the same or different and each represents H or an alkyl group containing 1 to 4 carbon atoms; and M^1 represents an L-valent metal), and
15 said treatment target substance has a moisture content of not higher than 500 ppm by mass.

2. The method for producing a stabilized fluoropolymer according to Claim 1,
20 wherein the sulfonic-acid-derived-group-containing fluoropolymer further contains $-\text{SO}_2\text{X}$ and/or $-\text{COZ}$ (wherein X represents F, Cl, Br, I or $-\text{NR}^5\text{R}^6$ and Z represents $-\text{NR}^7\text{R}^8$ or $-\text{OR}^9$; R^5 , R^6 , R^7 and R^8 are the same or different and each represents H, an alkali metal
25 element, an alkyl group or a sulfonyl-containing group and R^9 represents an alkyl group containing 1 to 4 carbon atoms).

3. The method for producing a stabilized
30 fluoropolymer according to Claim 1 or 2, wherein the sulfonic-acid-derived-group-containing fluoropolymer further contains $-\text{COOH}$ at the polymer chain terminus or termini.

35 4. The method for producing a stabilized

fluoropolymer according to Claim 1, 2 or 3,
wherein the fluorination treatment is carried out using
a gaseous fluorinating agent comprising a fluorine
source,

- 5 said fluorine source is at least one species selected
from the group consisting of F_2 , SF_4 , IF_5 , NF_3 , PF_5 , ClF
and ClF_3 and
said fluorine source amounts to not less than 1% by
volume of said gaseous fluorinating agent.

10

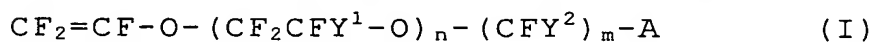
5. The method for producing a stabilized
fluoropolymer according to Claim 4,
wherein the fluorine source is F_2 .

15

6. The method for producing a stabilized
fluoropolymer according to Claim 1, 2, 3, 4 or 5,
wherein the sulfonic-acid-derived-group-containing
fluoropolymer is a copolymer which is at least binary
comprising

20

an acid-derived group-containing perhalovinyl ether
represented by the general formula (I):



- (wherein Y^1 represents F, Cl, Br, I or a perfluoroalkyl
group, n represents an integer of 0 to 3; n atoms/groups
25 of Y^1 are the same or different; Y^2 represents F, Cl,
Br or I; m represents an integer of 1 to 5; when m is
an integer of 2 to 5, m atoms of Y^2 are the same or
different; A represents $-SO_2X$ or $-COZ$; X represents F,
Cl, Br, I or $-NR^5R^6$ and Z represents $-NR^7R^8$ or $-OR^9$; R^5 ,
30 R^6 , R^7 and R^8 are the same or different and each represents
H, an alkali metal element, an alkyl group or a
sulfonyl-containing group and R^9 represents an alkyl
group containing 1 to 4 carbon atoms) and
a copolymerizable monomer with said acid-derived
35 group-containing perhalovinyl ether,

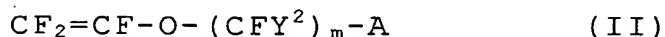
said copolymerizable monomer is an "other vinyl ether" other than said acid-derived group-containing perhalovinyl ether and an ethylenic monomer, said copolymer comprises 5 to 40 mole percent of an acid-derived group-containing perhalovinyl ether unit derived from said acid-derived group-containing perhalovinyl ether, 60 to 95 mole percent of an ethylenic monomer unit derived from said ethylenic monomer and 0 to 5 mole percent of an "other vinyl ether unit" derived from said "other vinyl ether".

7. The method for producing a stabilized fluoropolymer according to Claim 6, wherein n is 0 (zero).

15

8. The method for producing a stabilized fluoropolymer according to Claim 6 or 7, wherein Y^2 is F and m is 2.

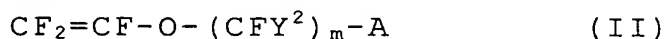
9. A stabilized fluoropolymer obtained via polymerization of an acid-derived group-containing perhalovinyl ether represented by the general formula (II):



(wherein Y^2 represents F, Cl, Br or I, m represents an integer of 1 to 5; when m is an integer of 2 to 5, m atoms of Y^2 are the same or different; and A represents $-SO_2X$ or $-COZ$; X represents F, Cl, Br, I or $-NR^5R^6$ and Z represents $-NR^7R^8$ or $-OR^9$; R^5 , R^6 , R^7 and R^8 are the same or different and each represents H, an alkali metal element, an alkyl group or a sulfonyl-containing group and R^9 represents an alkyl group containing 1 to 4 carbon atoms), and tetrafluoroethylene, wherein said stabilized fluoropolymer shows an intensity ratio [x/y] between carboxyl group-due peak

[x] and $-\text{CF}_2-$ due peak [y] of not higher than 0.05 in IR measurement.

10. A stabilized fluoropolymer obtained via
 5 polymerization of an acid-derived group-containing perhalovinyl ether represented by the general formula (II):



(wherein Y^2 represents F, Cl, Br or I, m represents an
 10 integer of 1 to 5; when m is an integer of 2 to 5, m atoms of Y^2 are the same or different; and A represents $-\text{SO}_2\text{X}$ or $-\text{COZ}$; X represents F, Cl, Br, I or $-\text{NR}^5\text{R}^6$ and Z represents $-\text{NR}^7\text{R}^8$ or $-\text{OR}^9$; R^5 , R^6 , R^7 and R^8 are the same or different and each represents H, an alkali metal
 15 element, an alkyl group or a sulfonyl-containing group and R^9 represents an alkyl group containing 1 to 4 carbon atoms) and tetrafluoroethylene, wherein, in a hydrolyzate of said stabilized fluoropolymer, the number [X] of main chain terminal
 20 $-\text{CF}_3$ groups per 1×10^5 main chain carbon atoms of said hydrolyzate is not smaller than 10 as calculated using an integrated intensity due to main chain terminal $-\text{CF}_3$ groups and an integrated intensity due to $-\text{CF}_2-$ adjacent to an ether bond in side chains branched from the main
 25 chain in said hydrolyzate, each determined by solid state ^{19}F nuclear magnetic resonance spectrometry of said hydrolyzate in a state swollen in an oxygen-containing hydrocarbon compound having a dielectric constant of not lower than 5.0 and further
 30 using an ion exchange equivalent weight Ew value determined by titrimetric method.

11. The stabilized fluoropolymer according to Claim 10,
 35 wherein said fluoropolymer further shows an intensity

ratio [x/y] between carboxyl group-due peak [x] and -CF₂- due peak [y] of not higher than 0.05 in IR measurement.

5 12. The stabilized fluoropolymer according to Claim 9, 10 or 11,
wherein the polymerization of the acid-derived group-containing perhalovinyl ether and tetrafluoroethylene is carried out in the manner of
10 emulsion polymerization.

 13. The stabilized fluoropolymer according to Claim 9, 10, 11 or 12,
which is obtained by the method for producing a
15 stabilized fluoropolymer according to Claim 7.

 14. A stabilized fluoropolymer,
which is obtained by the method for producing a stabilized fluoropolymer according to Claim 1, 2, 3,
20 4, 5, 6, 7 or 8.

 15. The stabilized fluoropolymer according to Claim 9, 10, 11, 12, 13 or 14,
which has a melt index of 0.1 to 20 g/10 minutes as
25 measured under the conditions of 270°C and a load of 2.16 kg according to JIS K 7210.

 16. A polymer electrolyte membrane,
which contains a hydrolyzate of the stabilized
30 fluoropolymer according to Claim 9, 10, 11, 12, 13, 14 or 15.

 17. The polymer electrolyte membrane according to Claim 16,
35 wherein the amount of fluoride ion eluted by Fenton

treatment comprising immersing b grams of said polymer electrolyte membrane in a liters of an aqueous hydrogen peroxide solution having an initial iron(II) cation concentration of 2 ppm and an initial hydrogen peroxide concentration of 1% by mass at a membrane/bath ratio [b/a] of 3.2 and maintaining the whole at 80°C for 2 hours is not greater than 11×10^{-4} parts by mass per 100 parts by mass of said polymer electrolyte membrane.

10 18. An active substance-immobilized material which comprises a hydrolyzate of the stabilized fluoropolymer according to Claim 9, 10, 11, 12, 13, 14 or 15 and an active substance.

15 19. The active substance-immobilized material according to Claim 18, wherein the active substance is a catalyst.

20 20. The active substance-immobilized material according to Claim 19, wherein the catalyst is a platinum-containing metal.

25 21. A membrane/electrode assembly comprising a polymer electrolyte membrane and an electrode, wherein said membrane/electrode assembly satisfies at least one condition selected from the group consisting of the conditions (1) and (2) given below:
 (1) said polymer electrolyte membrane is the polymer electrolyte membrane according to Claim 16 or 17, and
30 (2) said electrode is the active substance-immobilized material according to Claim 18, 19 or 20.

35 22. A solid polymer electrolyte fuel cell which comprises the membrane/electrode assembly according to Claim 21.